

Review

A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms

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Abstract

Boundary layers between different environmental compartments represent critical interfaces for biological, chemical and physical processes. The sea-surface microlayer (uppermost 1–1000 µm layer) forms the boundary layer interface between the atmosphere and ocean. Environmental processes are controlled by the SML, and it is known to play a key role in the global distribution of anthropogenic pollutants. Due to its unique chemical composition, the upper organic film of the SML represents both a sink and a source for a range of pollutants including chlorinated hydrocarbons, organotin compounds, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAH) and heavy metals. These pollutants can be enriched in the SML by up to 500 times relative to concentrations occurring in the underlying bulk water column. The SML is also a unique ecosystem, serving as an important habitat for fish eggs and larvae. Concentration ranges and enrichment factors of pollutants in the SML in different areas of the world's oceans have been critically reviewed, together with available toxicity data for marine biota found within the SML. Overall, the SML is highly contaminated in many urban and industrialized areas of the world, resulting in severe ecotoxicological impacts. Such impacts may lead to drastic effects on the marine food web and to fishery recruitment in coastal waters. Studies of the toxicity of fish eggs and larvae exposed to the SML contaminants have shown that the SML in polluted areas leads to significantly higher rates of mortality and abnormality of fish embryos and larvae.

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1. Introduction

The sea-surface microlayer (SML) represents the interface between the ocean and the atmosphere, where the transfer of material is controlled by complex physicochemical processes. This interface can serve as both a sink and a source of anthropogenic compounds, including chlorinated hydrocarbons, organotin compounds, petroleum hydrocarbons and heavy metals due to its unique chemical composition—in particular, its high content of lipids, fatty acids and protein. The SML plays an important role in the fate of persistent organic pollutants (POPs) in aqueous ecosystems (Southwood et al., 1999). Research into the accumulation of heavy

metals and POPs in the SML has been the focus of several studies over the last decade, but some processes and structure of the SML are still unknown (Liss and Duce, 1996). The SML is also an essential micro-habitat for a vast diversity of microorganisms (neuston), larvae and fish eggs. Exposure of the biota in the SML to residual pollutants has important implications with respect to the ecology of the wider marine environment. Such impacts are known to be particularly significant in polar regions where marine webs are relatively less complex (Corsolini et al., 2002).

This manuscript reviews available studies on the following SML pollutants: pesticides, polychlorinated biphenyls (PCBs), organotin compounds, petroleum hydrocarbons and heavy metals. The review summarizes key areas of knowledge with regard to these major pollutant types and associated physicochemical processes within the SML, with emphasis on knowledge deficits and requirements for further research on aspects of pollutant fate, transport and ecotoxicological impacts.

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2. Dimension and properties of the SML

The SML of the ocean is a complex and unique ecosystem, which comprises a series of sub-layers. Hunter (1980) described the transport processes of particulate matter in the SML and identified an upper hydrodynamic boundary layer with a thickness of $\sim 50\ \mu\text{m}$ within an SML of a $300\ \mu\text{m}$ total thickness. Hardy and Word (1986) defined three distinct layers: the surface nanolayer ($<1\ \mu\text{m}$) containing surface-active substances; the surface microlayer ($<10\ \mu\text{m}$) enriched with particles and microorganisms; and the surface millilayer ($<1000\ \mu\text{m}$)—the habitat for fish eggs and larvae. The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) used the following term of sub-layers for the SML (GESAMP, 1995): Viscous sub-layer ($<1000\ \mu\text{m}$), thermal sub-layer ($<300\ \mu\text{m}$) and diffuse sub-layer ($<50\ \mu\text{m}$). Zhang et al. (1998) described a multiple-layer model in which physicochemical properties of the SML change rapidly. The thickness of SML in the multiple-layer model was empirically determined as $50 \pm 10\ \mu\text{m}$ and further studies by Zhang et al. (2003) confirmed the thickness of the SML as approximately $60\ \mu\text{m}$ based on measurements using pH-microelectrode, but the thickness of the SML may change due to changing meteorological conditions and the organic matter composition of the SML.

Based on these scientific reports, the SML can be summarized as being a micro-habitat comprised of several layers distinguished by their ecological, chemical and physical properties with a total thickness of between 1 and $1000\ \mu\text{m}$. Based on the literature it is proposed that an SML of a thickness of $60\ \mu\text{m}$ could be meaningfully used for studying the physicochemical properties of the SML, and up to $1000\ \mu\text{m}$ for biological properties, depending the organism, or ecological features, of interest. Furthermore, it is suggested that a collected layer of surface water with a thickness of $>1000\ \mu\text{m}$ should be referred to as surface water, and not as SML, in order to distinguish between the SML and marine surface water.

2.1. SML sampling techniques

In the past 40 years, several techniques for sampling the SML have been developed. However, collection of SML samples of an acceptable integrity remains a challenge. Reasons for this are: (i) the SML is physically, chemically and biologically heterogeneous. For example, the thickness of SML changes according to wind speed, where wave motion may disturb or even destroy the SML. The chemical composition also is subject to rapid alteration in areas of natural slicks, where surface tension is higher; (ii) operation of sample techniques requires experience to collect samples with high reproducibility. For example, a study conducted by Knap

et al. (1986) reported a relative standard deviation (RSD) of 15% in the collected volume of SML among a group of ten scientists using a screen sampling technique (Garrett, 1965). A difference in sample volume led to a significant difference in the thickness of collected SML samples due to non-uniform withdrawal rate; (iii) the period of sampling may be excessive in order to collect a sufficient volume of SML sample for trace contaminant analysis. During the sampling period, the characteristics and concentrations of materials in the SML may change significantly.

Advantages and disadvantages of 21 different SML sampling techniques were reviewed initially by Hühnerfuss (1981a,b). The thickness of SML collected was found to be dependent on the technique deployed. The screen (Garrett, 1965), rotating drum (Harvey, 1966), glass plate (Harvey and Burzell, 1972) and teflon plate methods (Miget et al., 1974) are the most widely used SML sampling techniques used to date. Kjelleberg et al. (1979) compared hydrophilic and hydrophobic sampling devices to collect SML samples with respect to thickness. Carlson (1982) compared the glass plate and screen method, whereas Falkowska (1999a) and Falkowska (1999b) evaluated the glass plate, teflon plate and screen methods with respect to the thickness of SML collected. Falkowska (1999a), and Liu and Dickhut (1998) studied the effect of wind speed to the thickness of SML collected.

A manual procedure may be useful to ensure constant sampling condition and is given for the use of screen sampler by IOC (1985). Carlson et al. (1988) used a rotating glass drum to collect large volume of SML sample, whereas Hardy et al. (1988) used a teflon-coated drum. The material used as the sample carrier should be selected carefully, e.g. Stadler and Ziebarth (1975) pointed out that teflon contains extractable compounds which may disturb the gas chromatographic analysis of chlorinated hydrocarbons. Hardy et al. (1988) used a teflon drum sampler and extracted DDT from SML samples at a recovery of up to 88% in laboratory experiments using ^{14}C labeled DDT. Larsson et al. (1974) used a teflon plate, densely perforated with conical holes, to collect SML samples at the Swedish West Coast and reported concentrations of $\sum\text{DDT}$ and PCBs of 39 and $33\ \mu\text{g/l}$ respectively. Södergren et al. (1990) used a teflon disc to collect samples from SML in a water tank during laboratory experiments and found, after simulated atmospheric deposition of PCBs, a concentration of $7\ \mu\text{g/l}$ of PCBs in samples of SML. Mikhaylov (1978) used a nylon net to collect SML samples in the North Atlantic and stored samples in plastic bottles until analysis for pesticides. Concentrations of $11\ \mu\text{g/l}$ as total pesticides were reported based on analysis using thin-layer chromatography, whereas Larsson and Södergren used GC. The concentration levels reported by Larsson, Södergren and Mikhaylov

are higher by a magnitude of 100 compared to other studies (Table 1), and should be considered with caution due to sample techniques used, sample storage and the use of relatively unsophisticated analytical techniques.

The thickness of the SML sample collected with various devices also depends on a number of prevailing environmental factors at the time of collection including water temperature, the presence and density of surface slicks and, in the case of the drum sampler, the speed of rotation. The drum sampler permits collection of several liters of sample within 20–60 min, thereby minimizing risks of sample contamination. In general the thickness of SML collected by the glass plate method, or glass drum sampler, is consistent with the most recently reported actual thickness of SML of $50 \pm 10 \mu\text{m}$ (Zhang et al., 1998; Zhang et al., 2003). Overall, the drum sampler can be considered as the state-of-the-art SML sampling device, but questions remain as to whether water adhering to the drum dilutes the SML sample and whether there are compromises to sample integrity from device fabrication materials.

3. Persistent organic pollutants in the SML

3.1. Pesticides and PCBs

Pesticides and PCBs belong to the group of persistent organic pollutants (POPs) that represent a wide range of xenobiotic chemicals which are known to be recalcitrant and potentially toxic in the marine environment. There is increasing concern over the dispersion of POPs in the global environment and their impact upon wildlife (Jeminez, 1997; Jones and de Voogt, 1999). In particular, POPs have been implicated in causing adverse effects on endocrine systems in a wide range of marine organisms, including mammals (Tanabe, 2002; Bosveld and van den Berg, 2002).

Concentration levels of chlorinated hydrocarbons in the marine environment were reviewed by Fowler (1990). In summary, during the early 1970s to the early 1980s, reported PCB and DDT concentrations in the SML averaged <3.6 – 50 and <0.02 – 15 ng/l respectively in open oceanic water, and 1 – 235 and <0.05 – 39.9 ng/l at offshore sampling sites in the semi-enclosed Baltic Sea and Mediterranean Sea (Table 1). The results from early studies may be considered critically, but data from the mid-1980s can be viewed with more confidence due to the availability of more sophisticated analytical and sampling techniques, as well the awareness of sample contamination in trace analysis (Hillebrand and Nolting, 1987) to accumulate in the SML.

3.1.1. Open ocean

The concentration and enrichment factor (EF) of PCBs in the SML of oceanic waters have been reported

as 5 – 6 ng/l, $\text{EF} = 0.9$ – 3 (North Central Pacific; Williams and Robertson, 1973), 3.8 – 19.3 ng/l, $\text{EF} = 2.7$ – 20 (Sargasso Sea; Bidleman and Olney, 1974) and <1 ng/l (US Southeast coast, Blake Plateau, Gulf of Mexico; Sauer et al., 1989). The higher concentrations reported by Bidleman and Olney, and Williams and Robertson may reflect an improvement in analytical tools in recent years, or an actual decline in PCB levels in open ocean waters. Overall, the study from Williams and Robertson (1973) showed that at near shore locations along the Mexican and California coast, SML concentrations of PCB and DDT could be higher by factors of up to 10 and 40 respectively compared to oceanic water of the North Central Pacific. The levels of DDT residues reported in open oceanic waters were <0.02 ng/l (North Central Pacific; Williams and Robertson, 1973) and <0.05 – 0.5 ng/l (Sargasso Sea; Bidleman and Olney, 1974). Hexachlorocyclohexane (HCH) isomers α -HCH, β -HCH and γ -HCH (Lindane) were detected in the SML of open-ocean waters from the Sea of Japan and Barents Sea in a range of 0.92 – 1.75 , 0.15 – 0.44 , 0.40 – 1.59 and 0.33 – 0.51 , 0.11 – 0.17 , 0.32 – 0.45 ng/l respectively by Chernyak et al. (1995). The concentration of HCH-isomers was found to decline from the Sea of Japan toward the remote arctic region of the Barents Sea. Chernyak et al. (1995) reported EF values of 1.2 – 2 for HCH isomers, which are comparable with EFs for DDTs and PCBs reported for the North Central Pacific (Williams and Robertson, 1973). Lower EFs reported for pesticides and PCBs in the open ocean may be an artifact of rougher sea conditions during sampling, leading to physical disturbance and dilution of SML samples. Chernyak et al. (1996) carried out an investigation of contemporary pesticides (triazines, acetanilides, organophosphates and organochlorines) in the arctic regions of Bering and Chukchi. Only chlorthalonil and trifluralin were detected at the low concentrations of 0.2 and 1 ng/l respectively in the SML. In general, it has been observed by various researchers that only low concentrations of PCBs and pesticides are present in the SML of open oceanic waters. However, accumulation of PCBs and pesticides in the body lipids of marine organisms, by factors of up to 10^3 – 10^5 (Kennish, 1997) relative to surrounding marine water, means that even low concentrations of pollutants can lead to significant bioaccumulation.

3.1.2. Semi-enclosed water bodies

The concentration range for PCBs in the SML of the semi-closed Baltic Sea have been reported at 1.1 – 5.9 ng/l (Stadler and Ziebarth, 1976), 29.9 – 235.2 ng/l (Gaul and Ziebarth, 1980) and 5.5 – 46 ng/l (Mohnke et al., 1986). In the first two studies, a funnel method was used to collect a surface-layer of 3.5 mm, which is thicker by a factor of 8 and 35 compared to the screen and glass plate methods respectively. The samples were diluted by

Table 1
Concentrations and enrichment factors (EF) of DDTs, HCHs and PCBs in the sea-surface microlayer

Region	Year	Compound	Concentration (ng/l)	EF	References
Biscayne Bay, Florida Straits	1968	DDT residues	80–12710	80–12710	Seba and Corcoran (1969)
Narragansett Bay, Rhode Island	1972	\sum PCBs	450–4200	9–62	Duce et al. (1972)
North Central Pacific	1972	DDT residues	<0.02–15.4	<15	Williams and Robertson (1973)
		\sum PCBs	5.2–50	0.9–3	
Sargasso Sea	1973	DDT residues	<0.05–0.7	0.8–4	Bidleman and Olney (1974)
		\sum PCBs	<3.8–19.3	2.7–20	
Swedish West Coast	1972	DDT residues	39×10^6		Larsson et al. (1974)
		\sum PCBs	33×10^6		
Western Baltic Sea	1974	DDT residues	0.1–3.4		Stadler and Ziebarth (1976)
		\sum PCBs	1.1–5.9		
Western Baltic Sea	1976–1978	DDT	<0.05		Gaul and Ziebarth (1980)
		α -HCH	5.5–19.0	1.4	
		β -HCH	<0.02–1.3	0.6–3	
		Lindane	3.2–15.6	1.9–2.3	
		\sum PCBs	29.9–235.2	12–21	
Mediterranean Sea	1977	DDT residues	39.9		Mikhaylov (1979)
		DDD	9.2		
		DDE	13.2		
Rijeka Bay, Adriatic Sea, Croatia	1977–1981	p,p' -DDT	<1–12.5	1–39	Picer and Picer (1992)
		p,p' -DDE	0.2–8.1	0.2–93	
		p,p' -DDE	<0.1–4.7	0.5–16	
		\sum PCBs	1–597	2.2–59	
Blanca Bay, Argentina	1980–1981	o,p' -DDT	<3.6–100.7	0.1–21.3	Sericano and Pucci (1984)
		p,p' -DDT	<4–316.2	0.2–13.2	
		β -HCH	14.3–219.5	0.5–23.1	
Mediterranean Sea, Monaco	1981–1982	Lindane	3–7.8	4.6–780	Burns et al. (1985)
		\sum PCBs	3.2–35.9	15–49	
Mediterranean Sea, open water	1982	DDD	0.005	2.5	Burns and Villeneuve (1987)
		Lindane	0.05	25	
Baltic Sea and north-east Atlantic	1980–1984	DDT	0.22–17.9	<0.1–44	Mohnke et al. (1986)
		α -HCH	1.1–11.9	<0.1–8	
		β -HCH	0.16–3.46	<0.1–7	
		Lindane	1.40–32.4	<0.1–13	
		δ -HCH	0.06–0.68	<0.1–4	
		\sum PCBs	5.5–46.0	<0.1–59	
Los Angeles, California	1986	\sum DDT	47–179		Cross et al. (1987)
		Lindane	<1		
		\sum PCBs	8141–30708		
Atlantic Ocean and Gulf of Mexico	1989	\sum DDT	<0.2		Sauer et al. (1989)
		\sum PCB	<1		
Sea of Japan	1992	α -HCH	0.92–1.75	1.1–1.2	Chernyak et al. (1995)
		β -HCH	0.15–0.44	0.8–1.4	
		Lindane	0.40–1.59	0.9–4.7	
Barents Sea	1992	p,p' -DDT	<0.0006		Chernyak et al. (1995)
		p,p' -DDE	<0.0006		
		α -HCH	0.33–0.51	0.7–1.1	
		β -HCH	0.11–0.17	0.8–1.8	
		Lindane	0.32–0.45	1.4–1.5	
		\sum PCB	<0.001		
Alexandria, Egypt	1997	DDT	0.1–14	1.9–3.2	Abd-Allah (1999)
		DDD	0.1–28	1.7–2.7	
		DDE	1.9–45	2.3–3.0	
		Lindane	2.4–27	2.2–3.5	
		\sum PCBs	36.6–412.2	1.9–2.9	

sub-surface water during collection leading to an underestimation of concentration levels. Reported SML concentrations of DDT residues in the Baltic Sea of up to 3.4 ng/l were higher in 1974 (Stadler and Ziebarth, 1976) compared to later studies in 1976–1978, where concentrations of <0.05 ng/l were detected (Gaul and Ziebarth, 1980). Mohnke et al. (1986) detected DDT residues in the years 1980, 1981, 1983 and 1984 within a concentration range of 0.58–2.40, 0.41–2.71, 0.82–17.9 and 0.22–3.50 ng/l, which strongly indicates an underestimation of SML concentrations reported by Gaul and Ziebarth (1980). In the Mediterranean Sea DDT, DDD and DDE have been detected in a range of 10–89, 2.0–32.0 and 4.0–23.4 ng/l respectively in samples from SML collected by using a nylon net (Mikhaylov, 1979). Positive correlations between the concentration of petroleum hydrocarbons and DDD, DDE, DDT and HCCH in SML samples from the Mediterranean Sea have been observed (Mikhaylov, 1979), and Mohnke et al. (1986) suggested that petroleum hydrocarbons in oil films may act as 'extracting agents' for some organochlorines from sub-surface water to the SML. Therefore, petroleum hydrocarbons may positively accentuate the accumulation of organochlorines in the SML.

3.1.3. Coastal areas

More data are available for concentration levels in the SML of pesticides and PCBs in areas with high industrial, agricultural and shipping activities. Seba and Corcoran provided the first report of DDT levels in the range of 100–12710 ng/l in Biscayne Bay and the Florida Straits (Seba and Corcoran, 1969), which may indicate contamination of collected SML samples using the less accurate bottle method. Duce et al. (1972) showed a higher enrichment of PCBs between the SML and sub-surface water in areas sampled within visibly pronounced slicks compared to an area with less pronounced slicks in Narragansett Bay, Rhode Island. DDT residues have been detected in several parts of the world at high concentration ranges of 1.9–25.3 ng/l in 1981 (Rijeka Bay, Croatia; Picer and Picer, 1992), <4–416.9 ng/l in 1980/81 (Blanca Bay, Argentina; Sericano and Pucci, 1984), <1–442 ng/l in 1986 (Los Angeles, USA; Cross et al., 1987) and 1.6–87 ng/l in 1997 (Alexandria, Egypt; Abd-Allah, 1999). Hardy et al. (1987b) reported a total pesticide concentrations of <0.1–43.8 ng/l, but in general <5 ng/l of predominant benzene hexachloride isomers (BHC), aldrin and DDT were found in the SML of Puget Sound, USA. A range of other pesticides have been found in detectable concentrations in SML samples, e.g. Sericano and Pucci (1984) also detected high levels of DDT residue, Lindane, heptachlor and aldrin at 15.2–219.5, 6.9–389.5 and 4.1–853.2 ng/l respectively. The highest concentrations of these compounds were detected closest to the main sewer of the city Bahía Blanca and at the innermost

sample site of the bay. It was shown that SML concentrations of pesticide declined with distance from the coastline by a factor of up to 20 in sub-surface seawater, but less significantly in the SML by factor of only up to 5. The mean concentrations of DDTs and Dieldrin in the SML collected within Rijeka Bay, Croatia (Picer and Picer, 1992) declined from 5 and 0.7 ng/l respectively in coastal areas to 0.8 and 0.3 ng/l respectively 10 km seawards in the Adriatic Sea. This effect was even more significant for PCBs, which declined from 162 ng/l in the SML from coastal areas to 9.5 ng/l seawards. In the harbour of Los Angeles, the PCB concentration in the SML declined from the highly polluted area of Los Angeles of 30,000 to <13 ng/l 15 km seawards in the Pacific Ocean (Cross et al., 1987). The Σ DDT concentration also declined from 442 ng/l in the harbour to <1 ng/l in the Pacific Ocean.

Hardy et al. (1987b) reported much lower concentrations of pesticides and PCBs in SML samples (<0.1 and 28 ng/l respectively) collected in Sequim Bay and Central Sound around Puget Sound, compared to a polluted area in Elliot Bay and Commencement Bay of the Puget Sound (43.8 and 3894 ng/l respectively). Abd-Allah (1999) found the highest concentrations of 10 pesticides and metabolites in Alexandria, Egypt, at locations influenced by the discharge of wastewater from intensive industrial areas, surface run-off drainage from agricultural areas and harbour activities. DDT residues and Lindane were detected at 87 and 27 ng/l in the SML respectively with a corresponding EF of 2.5. At a distance of 2 km from the Monaco Coast in the north-eastern Mediterranean Sea, Lindane in SML samples was detected at 3–7.8 ng/l (Burns et al., 1985) and in the open waters of the Mediterranean Sea with 0.05 ng/l (Burns and Villeneuve, 1987). No significant influence of an incineration plant source in Nyborg, Denmark on contamination levels of POPs in the SML could be shown by Knulst and Södergren (1994), and the concentrations of total PCBs and total DDT were low at 4.9 and 1.6 ng/l, respectively.

Atrazine, a triazine herbicide was found at the highest concentrations of detectable pesticides in the range of 19–848 ng/l in the SML of estuarine areas in Winjah Bay, South Carolina (Kucklick and Bidleman, 1994). Atrazine has been used extensively in this area. Low enrichment factors of 1.0–1.4 of Atrazine were not consistent with enrichment factors reported of 1.6–110 in the SML of the Rhode River Atrazine by Wu et al. (1980) and Wu (1981). The higher enrichment of Atrazine reported by Wu (1981) and Wu et al. (1980) is likely to be due to differences in the organic composition of the SML resulting in different sorption characteristics. The octanol/water partition coefficient (K_{ow}) may be used as indicator for the enrichment of compounds in the hydrophobic SML and the lower log K_{ow} value of about 2.5 for Atrazine can be expected to result in a lower SML

enrichment (Kucklick and Bidleman, 1994) compared to DDT ($\log K_{ow} = 5.98$) and other common organochlorine pesticide which have $\log K_{ow}$ values higher than 3.6.

In general, the concentration of organochlorines in the SML of the open ocean are significantly lower than of coastal waters by factors of up to 100, 1000 and 30000 for HCB isomers, \sum DDT and \sum PCBs respectively. EF values can range between 2 and 100 in polluted areas. Industry, wastewater discharge and agricultural activities are the main sources for organochlorines, and atmospheric deposition and river run-off are likely the major ways for these compounds to the SML. The global distribution and fate of organochlorines through atmospheric transport via the process of global distillation are likely controlled in the oceanic environment via exchange process of the SML-atmospheric interface. Mathematical distribution and fate models considering the SML may give us a better understanding and more precise estimation for the global distribution of these compounds.

3.2. Organotin

Gucinski (1986) pointed to the potential importance of the SML as an accumulation and transport focal point for organotin, which originates mostly from antifouling paints. There are no data of TBT and their metabolites in the SML of open oceanic waters. However, Hardy and Cleary (1992) reported a decline of TBT concentrations in the SML from 50 ng/l in the harbour of Wilhelmshaven, Germany to 3.2 ng/l at a sampling point 280 km seawards in the North Sea. The concentrations of organotin compounds reported in the North Sea are lower than in other areas, including Chesapeake Bay (Hall et al., 1987; Matthias et al., 1988), England (Donard et al., 1986; Cleary and Stebbing, 1987) and Bermuda (Stebbing et al., 1990). However the concentrations of organotin compounds at the harbour and near shore sites were high enough to induce chronic or lethal effects to marine organisms. Stebbing et al. (1990) reported a decline of TBT concentrations of 41 ng/l in the SML from Hamilton Harbour, Bermuda seawards to 0.9 ng/l.

Donard et al. (1986) reported that the monobutyl tin (MBT), a degradation product of TBT, was more widespread in sub-surface waters and the SML than TBT in the Great Bay Estuary, England. The fact that no DBT was detected supports the probability of rapid decomposition of DBT in environmental waters. In contrast, Matthias et al. (1986, 1988) found that TBT and DBT were more abundant, and present at higher concentrations compared to MBT in the northern Chesapeake Bay, USA. Matthias et al. (1988) reported the highest concentrations of TBT in SML and sub-surface waters of up to 4130 and 367 ng/l, respectively at sampling locations inside marinas. The concentrations

of DBT and MBT declined with degradation in SML up to 1650 and 1010 ng/l respectively, and to 233 and 102 ng/l respectively in subsurface water. In general, the tendency of decreasing concentration levels in the SML and sub-surface waters of degradation product with the progress of degradation was consistent (Matthias et al., 1988). MBT and DBT are more highly charged and therefore more hydrophilic leading to a depletion of MBT and DBT in the SML relative to TBT. However, the non-charged tetrabutyl-tin (TTBT) could not be detected, which is consistent with results reported by Matthias et al. (1986) and Hall et al. (1987).

Hall et al. (1987) reported higher concentrations of DBT and TBT in the SML and sub-surface water at sampling locations within marinas compared to levels in a harbour and major shipping channel. EF values ranged between 1.5 and 8 in marinas with a maximum concentration for TBT and DBT in the SML of 1050 and 1170 ng/l respectively. A significant increase of concentration in the months April to June was observed when most newly painted boats were being launched into the water. Concentrations decreased in the late autumn and winter. Cleary and Stebbing (1987) also reported high concentrations of organotin in SML and sub-surface water in the months May and June in Southwest England. In general the elevated concentrations were only found in marinas and not at sampling locations in rivers, offshore and mayor shipping lanes (Cleary and Stebbing, 1987; Hall et al., 1987; Matthias et al., 1988). The major source of TBT and its metabolite in the SML and seawater were associated with boating activities in marinas, and there was no evidence of a significant increase in concentrations from commercial shipping activities. Typical EF values ranged from 2 to 35 (Table 2). Concentrations in marinas of up to 4000 ng/l are capable of causing chronic and acute effects on marine organisms (Huggett et al., 1992; Hoch, 2001).

3.3. Polycyclic aromatic hydrocarbons and hydrocarbons

3.3.1. Polycyclic aromatic hydrocarbons (PAHs)

In general, high concentrations of PAHs in the SML have been found at sampling locations associated with anthropogenic coastal activities, particularly shipping harbours (Cross et al., 1987; Hardy et al., 1990; Kucklick and Bidleman, 1994; Zeng and Vista, 1997; Cincinelli et al., 2001). For example, the total concentration of PAHs in the SML in the harbour of Los Angeles was up to 55 μ g/l (Cross et al., 1987), in Baltimore up to 6 μ g/l (EF = 376) (Hardy et al., 1990), in Georgetown (South Carolina) up to 2.8 μ g/l (mean EF = 17.9 ± 35.9) (Kucklick and Bidleman, 1994) and in San Diego up to 1.4 μ g/l (Zeng and Vista, 1997). The concentrations declined from the harbour of Los Angeles to sampling locations 8 and 15 km offshore to 40 and 35 ng/l respectively (Cross et al., 1987). A decline of total PAHs

Table 2

Concentration and enrichment factors (EF) of organotin compounds in the sea-surface microlayer

Region	Year	Compound	Concentration (ng/l)	EF	References
Chesapeake Bay, Maryland	1986	MBT	165	>165	Matthias et al. (1986)
		DBT	91 and 150	11 and 15	
		TBT	1872	>1872	
Great Bay Estuary, England	1986	MBT	42–212	1–30	Donard et al. (1986)
		TBT	<0.2–306	>1530	
Chesapeake Bay, Maryland	1985	DBT	<10–1156	0.1–>112	Hall et al. (1987)
	1986	TBT	<24–1171	0.1–35	
Southeast England	1986	Organotin	24–1069	1.9–27	Cleary and Stebbing (1987)
Chesapeake Bay, Maryland	1988	MBT	5–1005	0.4–9.8	Matthias et al. (1988)
		DBT	8.5–1650	0.3–7.1	
		TBT	60–4130	0.8–11.2	
Bermuda	1988	DBT + TBT	40–429	1–2.9	Stebbing et al. (1990)
		TBT	15–307	1.5–34	
German Bight	1990	TBT	3.2–50.5	2–10.7	Hardy and Cleary (1992)
		Organotin	9.6–77	3–16.5	

concentration of 333 ng/l (EF = 198) in the harbour of Leghorn, Italy to 0.214 ng/l (EF = 3.4) at a sampling location 33 km offshore was reported by Cincinelli et al. (2001). By comparing the data of Cross et al. (1987), Hardy et al. (1990), Zeng and Vista (1997) and Cincinelli et al. (2001), it can be concluded that the total concentration of PAHs in SML increases generally with the size of the port and intensity of shipping traffic. Discharge of waste water from shipping combined with limited water exchange in a harbour is the main cause of PAHs contamination. However reported concentrations of Σ PAHs in the SML of Puget Sound, Washington of up to 8031 $\mu\text{g/l}$ (mean concentration = 132 $\mu\text{g/l}$) are higher by two orders of magnitude than levels reported by Cross et al. (1987) in the port of Los Angeles, California.

Anikiev and Urbanovich (1989) collected samples from the SML and subsurface in various oceans of the world. Mean concentrations of total petroleum hydrocarbons in the SML for the North Atlantic, Mediterranean Sea, Red Sea and Indian Oceans were 300, 310, 13 and 200 $\mu\text{g/l}$ respectively, whereas the mean concentrations in the sub-surface waters were 310, 80, 127 and 100 $\mu\text{g/l}$ respectively. No enrichment was observed in the SML of the North Atlantic and Red Sea, most probably due to the rough sea condition and destruction of the SML at the time of sample collection. The highest mean concentrations of peroxide, a product of the photo oxidation of PAHs, was measured at 134 $\mu\text{g/l}$ in the SML (EF = 5.5) in the Red Sea, where high UV intensities most probably resulted in the high concentration. Concentration of PAHs in the SML for the semi-enclosed Baltic Sea were 53.3 ng/l for the western Baltic Sea, 23.1 ng/l for the central Baltic Sea and 5.6 ng/l for the northern and eastern part of the Baltic Sea closed to Sweden and Finland. The western Baltic Sea is more

affected by river run-off from industrial areas and shipping traffic compared to the seas offshore of Sweden and Finland in the north. The key sources for PAHs in the SML offshore are derived from atmospheric particulate deposition. In the western Baltic Sea EF values of up to 12 were reported, whereas the EF values in the northern and eastern Baltic Sea were only 1.8.

In general, relatively high concentrations of PAHs in the SML have been detected in marine embayments, most likely due to the proximity of the contamination source and restricted hydrodynamics. Hardy et al. (1987b) reported concentrations of total PAHs in the range of 0.04–8000 $\mu\text{g/l}$ in Puget Sound, Washington, where the highest concentrations were found close to urban areas, and in samples collected within visible surface slicks. Hardy et al. (1990) reported a range of total PAHs in the SML of Chesapeake Bay between 65 and 3142 ng/l. The bay is characterized by run-off from large rivers, the Chesapeake Delaware Canal, as well as urban catchments. The lowest concentrations were found at the mouth to the North Atlantic and increased to the northern inner part of the bay. In the Winjah Bay, South Carolina (Kucklick and Bidleman, 1994) the concentration of total PAHs in the SML were below of 0.2–409 ng/l within the bay—lower than levels reported for in Chesapeake Bay (Hardy et al., 1990), although in the study of Kucklick and Bidleman (1994) a thicker SML of 332 μm was collected versus 50 μm (Hardy et al., 1990).

Kucklick and Bidleman (1994) used the ratio of methylphenanthrenes to phenanthrene (MP:P) (Takada et al., 1990, 1991) to identify sources of contaminations in the SML. The mean ratio of 0.47 ± 0.20 in Winjah Bay suggested run-off and/or atmospheric fallout of urban dust as the main sources of PAHs, and not used

motor oil discharged via the surface drainage system. The same conclusion was reached by Zeng and Vista (1997) for samples collected in San Diego Bay, California using concentration ratios of phenanthrene to anthracene (P:A), fluoranthene to pyrene (FL:PYR) and benzo(a) anthracene to chrysene (BZ(a):CHR) (Colombo et al., 1989). SML samples from the harbour of Los Angeles (Cross et al., 1987) showed high P:A ratios of >3.5, suggesting a source of unburned petroleum products, but contrary low FL:PYR ratios of <1 for same samples indicated combustion residues as the key contaminants. A low ratio of FL:PYR suggested combustion residues as the origin of PAHs in the SML collected in Chesapeake Bay (Hardy et al., 1990). A low ratio of <1 of the low to high molecular weight PAHs (LMW:HMW) in SML samples from the Oder River outflow indicated a pyrogenic origin of PAHs for the Baltic Sea (Witt, 2002). Samples from the SML were collected close to an oil-rig platform near the Montebello Islands 80 km from the northwest coast of Australia (Burns and Codi, 1999). The concentration of

total PAHs in the SML was 1576 µg/l with an uncommonly high EF value of 218 from the platform in the direction of tidal flow. However the ratio FL:PYR was <1 indicating combustion residues as the contaminant source, although direct contamination from petroleum may have been expected close to the platform.

3.3.2. Hydrocarbons

Concentration ranges of total alkanes of 0.097–1, 1.23–3674 and 21.2–245 µg/l were reported for the Northern Adriatic Sea (Marty et al., 1988), Leghorn, Tyrrhenian Sea (Cincinelli et al., 2001) and Chesapeake Bay, Washington (Hardy et al., 1990). The concentration of total alkanes in the particulate fraction increased along a transect from Istrian Peninsula towards the Po River Estuary in the Adriatic Sea (Marty et al., 1988). The increasing concentrations may be assigned to the particulate load of the Po River and the confined hydrological conditions of the basin. A carbon preference index (CPI) (Marty et al., 1988) of 1.2–1.6

Table 3
Concentration and enrichment factors (EF) of hydrocarbons and PAHs in the sea-surface microlayer

Region	Year	Compound	Concentration (µg/l)	EF	References
Istrian Peninsula (Croatia)/Po River Estuary (Italy)	1980–1982	$\sum n$ -alkanes, diss. $\sum n$ -alkanes, part.	0.13–1 0.1–1	0.7–3.1 2–32	Marty et al. (1988)
Mediterranean Sea, Monaco	1981–1982	Petroleum hydrocarbons	14.6–47.2	21–79	Burns et al. (1985)
Mediterranean Sea	1982	Petroleum hydrocarbons	19	1.9	Burns and Villeneuve (1987)
North Atlantic	1982	Petroleum hydrocarbons	80–690	1	Anikiyev and Urbanovich (1989)
Mediterranean Sea	1983	Petroleum hydrocarbons	60–240	3.9	
Red Sea	1983	Petroleum hydrocarbons	10–20	0.1	
Indian Ocean	1983	Petroleum hydrocarbons	10–810	2	
Puget Sound, Washington	1985–1986	\sum PAHs $\sum n$ -alkanes (C ₈ –C ₃₄)	1–8031 2–2057		Hardy et al. (1987b)
Los Angeles, California	1986	\sum PAHs	0.035–55.8		Cross et al. (1987)
Chesapeake Bay	1986	$\sum n$ -alkanes (C ₁₀ –C ₃₄), part. \sum PAHs	21.2–245 0.07–6	33 196	Hardy et al. (1990)
Winjah Bay, South Carolina	1990	\sum PAHs	0.0015–2.9	1.4–34	Kucklick and Bidleman (1994)
San Diego, California	1994	\sum PAHs, part. \sum PAHs, diss.	0.02–1.44 <0.035–0.042	50	Zeng and Vista (1997)
Montebello Islands, Australia	1999	\sum PAHs	1.6	218	Burns and Codi (1999)
Baltic Sea	1992–1998	\sum PAHs	0.0045–0.053	1.6–12	Witt (2002)
Leghorn, Italy	1999	$\sum n$ -alkanes (C ₁₄ –C ₃₄), diss. $\sum n$ -alkanes (C ₁₄ –C ₃₄), part. \sum PAHs, diss. \sum PAHs, part.	0.4–1.8 0.4–410 0.2–15.2 0.8–154	1.4–2.9 0.4–73 1.4–40 1.5–113	Cincinelli et al. (2001)

suggested a low input of naturally derived terrestrial alkanes. The CPI value for 32 of 36 samples collected from the SML in Chesapeake Bay, Washington (Hardy et al., 1990) varied between 5 and 33—strongly indicating biogenic sources in this area. Four samples showed a CPI value of <5 indicating possible contamination by petroleum hydrocarbons. The total PAH concentration in the particulate fraction was higher by a factor of up to 125 compared to the dissolved fraction in SML samples collected in the harbour of Leghorn, Italy (Cincinelli et al., 2001). In general high concentrations of Σ PAHs are associated with shipping traffic and anthropogenic activities in harbours. Atmospheric deposition of combustion residues and biogenic sources may lead to the enrichment of Σ PAHs in the SML in less polluted areas. Reported EF values for Σ PAHs vary between two offshore in the Baltic Sea to up to 200 at polluted areas (Table 3).

4. Metal pollutants in the SML

Early studies of heavy metals in the SML were reviewed by Hardy (1982) and in the marine environment by Fowler (1990). Hunter (1996) pointed out that concentration data published for metal trace analysis in the 1970s should be used with caution due to unsophisticated sampling and analytical techniques used at the time. Concentration levels in the SML and sub-surface water of the heavy metals Cu, Cd, Hg, Zn and Pb are summarized in Table 4. Heavy metals are enriched in the SML as dissolved and particulate fraction by factors of 1.3–5 and 2–100 respectively.

The concentration of heavy metals normally decrease with distance from the coastline (Cross et al., 1987; Hardy and Cleary, 1992). Dissolved organic ligands and particulates control the enrichment of the corresponding fractions. The mechanism of enrichment of heavy metals in the SML is very complex and Hunter (1996) suggested that the SML may accumulate micro-particulates (colloidal particles), as indicated by a greater ratio of protein:carbohydrate in the SML than in sub-surface waters. Hunter and Liss (1981) suggested that dissolved metals could be enriched by metal-ion complexation with organic ligands enriched in the SML. The enrichment and fractionation of heavy metals in the SML depends on many factors including organic matter composition of the SML, pH, salinity and binding affinities of heavy metals. Cadmium does not bind strongly to organic compounds in seawater to form organic complexes (Sadiq, 1992), which is in general consistent with the higher dissolved concentration of Cd in the SML and sub-surface water reported by Cross et al. (1987), Hardy et al. (1990), Hong and Lin (1990) and Brüggemann et al. (1992). The presence of Fe hydroxides play a major role in the formation of inorganic partic-

ulates of Pb. Cross et al. (1987) reported increasing concentration of particulate Pb in the SML with an increasing concentration of particulate Fe. The enrichment of total concentrations of Pb increased with increasing enrichment of Fe in the SML of the Chesapeake Bay, Washington (Hardy et al., 1985) indicating that Pb in the SML may be associated primarily with Fe-rich atmospheric matter and dust. Marty et al. (1988) and Garabetian et al. (1993) showed that the organic matter phase of the SML is characterized by an enrichment of hydrocarbons and surface activity. However the composition of organic matter may be expected to change significantly with location due to the influence of the activity of bacteria and plankton, anthropogenic sources of organic matter and prevailing hydrodynamic conditions.

Pellenberg and Church (1979) reported that bacteria can release organic compounds which may effect chelation of dissolved trace metals in the SML collected in the salt marsh of Delaware. However, Lion et al. (1982) reported negligible dissolved organic carbon (DOC) and dissolved trace metals enrichment in the SML of an estuarine salt marsh in the San Francisco Bay. Beside pack ice melting, uptake process during a bloom of phytoplankton was linked to a peak concentration of particulate Cu in the seawater of Antarctica, which may have contributed to a particulate concentration of Cu in the SML of 0.06 $\mu\text{g/l}$ (Grotti et al., 2001). This level is relatively high compared to the concentration range reported in the Baltic Sea of 0.001–0.90 $\mu\text{g/l}$ (mean concentration = 0.037 $\mu\text{g/l}$) by Brüggemann et al. (1992).

Hardy et al. (1985) investigated the heavy metal enrichment in the SML in an urban and rural area in the bay of Puget Sound, Washington and reported that concentrations of Pb, Zn and Cu in the SML were higher by factors of 2–15 in urban area, but no differences were reported for Cd. Hardy et al. (1987b) reported heavy metal concentrations being higher by up to 500 times in the same urban area as in a previous study (Hardy et al., 1985) and identified “hot spots” of contamination, particularly in areas of slicks. Hong and Lin (1990) reported that the content of dissolved organic matter (DOC) was enriched in the SML compared to sub-surface waters ($\text{EF} = 1.33$) in Jiulong Estuary, China. DOC accounted for between 70% and 80% of total organic matter (TOC) in SML samples leading to a predominance of Cu and Cd in the dissolved fraction. The dissolved fraction of heavy metals in the SML and subsurface water dominated in the Baltic Sea (Brüggemann et al., 1992) indicating the dominance of dissolved fractions in open and semi-enclosed seas, where particulates are less abundant. Hardy et al. (1990) reported in general a higher particulate fraction of heavy metals compared to the dissolved fraction in the SML for samples collected in the Chesapeake Bay, Washington. The water exchange in the Chesapeake Bay is less

Table 4
Concentration and enrichment factors (EF) of heavy metals in the sea-surface microlayer

Region	Year	Metal	Concentration ($\mu\text{g/l}$)			EF			References
			Total	Particulate	Dissolved	Total	Particulate	Dissolved	
Puget Sound, Washington	1982/1983	Cd	<0.02–1			6–8			Hardy et al. (1985)
		Cu	4–28			10–16			
		Pb	2–31			26–65			
		Zn	15–71			14–29			
Puget Sound, Washington	1985/1986	Cd	0.1–2.7						Hardy et al. (1987b)
		Cu	1.3–3215						
		Pb	<0.02–655						
		Zn	<5.1–1417.1						
Los Angeles, California	1986	Cd		<0.01–0.36	0.06–3.08				Cross et al. (1987)
		Cu		0.19–101	0.65–18.3				
		Pb		<0.07–100	0.11–1.30				
		Zn		<0.18–457	2.36–124				
Chesapeake Bay	1986	Cd	0.11–0.2	0.05–0.16	0.04–0.09	0.4	9	0.2	Hardy et al. (1990)
		Cu	4.2–16.2	1.76–13.2	1.1–3	8	>62	1.6	
		Pb	4.9–24.2	4.73–23.7	0.21–1	43	105	4.7	
		Zn	18.9–58.9	9.7–26.9	9.2–32	2.6	>45	1.5	
		Hg	0.003–0.14	0.0007–0.013	0.001–0.003	4.2	>72	1.3	
Baltic Sea	1984	Cd		<0.0001–0.03	0.001–0.1		5.7	1.5	Brügmann et al. (1992)
		Cu		0.001–0.9	<0.001–2.2		4.2	1.5	
		Pb		0.004–0.3	<0.001–0.4		3.6	2.2	
		Zn		0.015–0.8	0.2–5.8		4.1	2	
		Hg	<0.00002–0.06			4.5			
Xiamen Bay, China	1987	Cd	0.02–0.08	0.007–0.013	0.02–0.03	1.1–1.6	0.89–1.9	1.1–1.6	Hong and Lin (1990)
		Cu	0.6–2.3	0.4–1	0.9–1.3	1–2.61	1.2–6.5	1.2–1.5	
German Bight	1990	Cd	0.018–18.4			1.6–2.7			Hardy and Cleary (1992)
		Cu	1.4–4.7			1.9–8.7			
		Pb	0.77–2.07			1.9–6.1			
		Zn	10.2–20.5			1.1–4.7			
North-western Mediterranean Sea	1994	Cd	4.8			55			Migon and Nicolas (1998)
		Pb	1.2–6.5			19			
Western Ross Sea, Antarctica	1997–1998	Cu		0.06		1.6			Grotti et al. (2001)

intensive and high volumes of river run-off may contribute to a particulate concentration in the SML which generally range between 10 and 197 mg/l compared to a 0.07–2.61 mg/l in the Baltic Sea (Brüggmann et al., 1992).

The concentration of total dissolved Zn, Pb and Cu was dominant in the SML in the North Pacific 15 km offshore of the harbour of Los Angeles and decreased significantly to the harbour, whereas the particulate fractions increased by a factor of up to 2500 towards the harbour (Cross et al., 1987). However, minor particulate fractions in subsurface water compared to the SML was observed for Cu, Pb, Cd, Zn and Hg (Hardy et al., 1990) indicating a major role of floating particulates on the surface in scavenging heavy metals.

Data for Hg in the SML are limited, Brüggmann et al. (1992) reported a total mean concentration of Hg in the SML of 25 ng/l (EF = 4.5). Sadiq (1992) proposed that adsorption of Hg is not an important scavenging mechanism for Hg in seawater and Hardy et al. (1990) showed negligible concentrations of particulate Hg in sub-surface waters in Chesapeake Bay, Washington, however, a considerable fraction of particulate Hg of between 21% and 89 % in the SML were reported, where total concentration ranged between 2.9 and 14.2 ng/l in the SML.

It can be concluded that dissolved organic matter and particulates control the enrichment of heavy metals in the SML, and EFs can range between 2 and 100. Concentrations of heavy metals in polluted areas can be higher by a magnitude of 1000 in the SML compared to reported background concentrations in seawater (Table 5). In polluted areas, high concentrations of particulates result in a predominance of heavy metals in the particulate fraction, whereas the dissolved fraction of heavy metals is significantly higher in open or semi-enclosed seas. The complexation of metals to organic ligands and particulates is complex, and binding affinities effect the enrichment factor in the SML. Further studies on the effect of organic matter in the SML would lead to a better understanding of enrichment processes of heavy metals in the SML.

5. Toxicity

The SML provides a habitat for marine biota, including fish eggs and the larvae of many commercial fish species. Bacteria, micro-algae and invertebrates are commonly enriched by factors of 10^2 – 10^4 , 1 – 10^2 , and 1 – 10 respectively in the SML. The accumulation of organic pollutants and heavy metals in the SML leads to ecotoxicological impacts to the neustonic community including mortality, developmental abnormalities, depression of grow rates and prolonged hatch time of fish eggs.

The SML was found to be significantly more toxic than the sub-surface water for turbot eggs (Von Westernhagen et al., 1987), for atlantic cod eggs (Kocan et al., 1987), echinoderm larvae (Hardy and Cleary, 1992), clam larvae, but less so for oyster larvae (McFadzen and Cleary, 1994). A decline of toxicity (as a percentage of mortality, abnormalities or reduced growth) in the SML from polluted to less polluted areas was reported for kelp bass larvae in Los Angeles, USA (Cross et al., 1987), for clam and oyster larvae in the North Sea (McFadzen and Cleary, 1994; Hardy and Cleary, 1992), for echinoderm and copepods larvae in the North Sea (Hardy and Cleary, 1992), and atlantic mackerel, window-pane flounder and winter flounder in New York Bight, as well as the mid and north Atlantic (Longwell et al., 1992). Hardy and Cleary (1992) and McFadzen and Cleary (1994) reported negative correlations of Cu, Pb, TBT and organotin concentrations to the survival rates of clam and oyster larvae. Although these correlations do not prove cause and effect, they provide a strong indication of a significant effect on the larval stage of marine bivalves. However, it was suggested that no single contaminant or group of contaminants were obvious candidates for the toxicity of the SML in Puget Sound, Washington, but rather a synergistic effect all contaminants probably induced high toxicity (Hardy et al., 1987b).

Toxicity tests in a series of dilution of collected SML samples suggested that toxicity was due to heavy metals (Von Westernhagen et al., 1987), where toxicity increased at lower salinities via an increase in concentrations of free metal ions (Verslycke et al., 2003; Blackmore and Wang, 2003). However, Cross et al. (1987) stated that chemical analysis may not be a good predictor of toxicity. Kocan et al. (1987) reported a lower hatching success for Atlantic cod (48%) in the SML within a visible slick compared to 76–84% in the SML collected outside of slicks from the inner harbour of Helgoland, North Sea. SML from slicked areas is often to be found more toxic (Kocan et al., 1987; Hardy et al., 1987a; Rumbold and Snedaker, 1999) due to the higher enrichment of heavy metals and organics. The percentage of abnormal hatches for herring eggs in the North Sea and Baltic Sea were 28% and 18% respectively, and

Table 5
Background concentrations of heavy metals in seawater

Metal	Background concentration ($\mu\text{g/l}$)
Cadmium	10^{-3a} , 10^{-3} – 10^{-4b}
Copper	$<0.1^a$
Lead	0.1^a
Zinc	$<1^c$
Mercury	2×10^{-2a} , $<2 \times 10^{-3b}$

^a Sadiq (1992).

^b Fowler (1990).

^c Kennish (1997).

for turbot eggs 14% and 100% respectively (Von Westernhagen et al., 1987) indicating different sensitivities to SML contaminants among species. Herring eggs were sensitive to the presence of high concentrations of heavy metal, whereas turbot eggs were not, but showed higher sensitivity to samples with high concentrations of petroleum hydrocarbons.

The brine shrimp *Artemia* spp. showed a typical dose-response after exposure to SML for samples collected in the coastal area of Nyborg, Denmark, but in contrast the brackish water crustacean *Nitrocras spinipes* (Knulst and Södergren, 1994) did not. Studies from Von Westernhagen et al. (1987) and Knulst and Södergren (1994) also showed that different species may respond differently to contaminants in the SML. Riznyk et al. (1987) showed that the phyto-neuston in the SML could adapt to toxic levels of fluoranthene after four days indicating a high adaptive capacity of certain species to organic contaminants. Concern has been raised regarding potential toxicity of the SML as a habitat for fish eggs and larvae (Hardy et al., 1987a; Von Westernhagen et al., 1987; Longwell et al., 1992; Rumbold and Snedaker, 1999).

Lower hatching success and malformation of larvae has been frequently reported for SML samples collected in polluted areas. It was suggested that the levels of contaminants present in the SML, and the probability of toxic effects to the neuston community, could present a serious threat for the recruitment of juvenile fish stocks in the North Sea (Hardy and Cleary, 1992). However species response to SML contamination was found to be variable.

6. Conclusions

A wide spectrum of chemical contaminants are known to accumulate in the SML due to unique chemical composition, with potentially high enrichment of contaminants relative to underlying marine waters. The SML is an important habitat of the neustonic community including fish eggs and larvae, enrichment of contaminants, by up 1500 times relative to the subsurface water, can lead to severe ecotoxicological impacts to the neustonic community. Sources of SML contaminants in the marine environment can be mainly attributed to terrestrially derived wastewater discharges, agricultural and industrial run-off, atmospheric deposition of combustion residues, and shipping activities. In general, enrichment factors of pollutants in the SML are significantly lower in the open ocean and semi-enclosed seas (ranging between 0.8 and 5) relative to coastal and estuarine marine waters, as well as enclosed embayments, harbours and marinas where EF values of up to 1500 have been reported. Industrial harbours, in particular, are associated with high concentration of organochlorines, PAHs and heavy metals in the SML which

are known to induce chronic and acute effects on marine organisms. Toxic concentrations of organotin compounds in the SML are particularly associated with in marinas, sport boat and yachting activities. Variations in the organic composition of the SML is most likely linked to complex mechanisms responsible for the accumulation and scavenging of heavy metals in the SML. Due to the heterogenous nature of the SML it is challenging to compare concentration of pollutants from different regions, or even at different times from a single location. It is imperative that a standard procedure be adopted to minimize potential sources of sampling error. It is recommended that this procedure based on the use of either the glassplate or glass drum sampler techniques. These sampling techniques collect SML samples with a thickness of $50 \pm 10 \mu\text{m}$, which is consistent with the most recent empirically derived measurement of the actual thickness of the SML of $60 \mu\text{m}$ under calm sea conditions.

For comparative studies, it is critical that a standard sampling protocol for SML sampling be adopted. A standard procedure for collection of the SML would not only ensure consistency in the operation of the sampler device, but also ensure collection of SML samples only under suitable prevailing environmental conditions. The calculated thickness of the collected SML with respect to sample volume, sample collection surface area of the device and exact sampling time should be reported. Prevailing environmental parameters at the time of SML sample collection should also be recorded including wind speed, surface tension, temperature and tidal status. On-going activities, which may influence the characteristics of the SML, in the vicinity of the sample collection site should also be noted. By observing strict sampling and recording protocols during SML sampling, greater assurances could be achieved with respect to the comparison of SML contaminant data, both on the temporal and spatial scales.

It is clear from the many studies conducted on the measurement and behaviour of contaminants in the SML, that this layer of the ocean plays a critical role in the global distribution of persistent organic pollutants, but its precise significance remains uncertain. New approaches to modeling the transfer of contaminants between the SML-atmospheric interface need to be established in order to establish the SML's significance in controlling mass transfer of pollutants across the interface, and to yield new insights into the fate and transport of POPs within the global context. The partitioning of pollutants between the dissolved and particulate fraction within the SML is still largely unknown, and studies on the physicochemical processes which result in the exchange of POPs between the overlying atmosphere and underlying water column are justified.

A greater understanding of the size distribution of particles within the SML holds the key to understanding

the process of particle enrichment and associated pollutants. For example, further study on the specification of metals in the SML is needed in order to provide greater insight into the bioavailability of toxic elements and their impacts on the neustonic community. Furthermore, it is still unknown to what extent photochemical processes affect the behaviour of pollutants, such as PAHs, within the SML relative to sub-surface waters. Such processes may lead to both the destruction of POPs and the creation of toxic byproducts, both of which have important ecotoxicological implications.

Overall, it is clear that the quality of the SML has been degraded in coastal regions of the world that have been impacted by human development. It is likely that the rapidly industrialization of tropical regions, including much of Asia and southern China, is currently having a major impact on levels of contaminants in the SML, and this can be anticipated to escalate into the future. The tropics are suspected to be a major source of pollutants for the long range atmospheric transport of POPs globally, but the exact role of the SML as the interface for pollutant exchange between the ocean and atmospheric systems remains unknown. A more holistic approach to research on the intrinsic physicochemical and biological processes of the SML is justified in all regions of the world to enhance our understanding of this important environmental interface and its exact role in the global distribution of anthropogenic contaminants.

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